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LIGHT SENSITIVITY OF CUPROUS OXIDE AND OF SELENIUM.

DISSERTATION
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BY

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177,124

LIGHT SENSITIVITY OF CUPROUS OXIDE AND OF SELENIUM.

Introduction.

The light sensitivity of cuprous oxide and of selenium has been tested in the following three ways: first, by measuring the change in the electrical resistance produced by light; second, by measuring the change in the potential of the substance produced by light, when the substance is used as one plate in an electrolytic cell, that is by obtaining the photo-electrolytic action; and third, by measuring the potential of the substance produced by light, when the substance is placed in the field of a positively charged cylinder, in a vacuum, that is, by obtaining the photo-electric effect.

In the present investigation, these three effects have been measured on the same sample, since different samples have been found to vary greatly in their sensitivity. Also, the work on the photo-electrolytic action has been extended, by measuring the effect of the different wave-lengths, in the region 8700 to 2600 A.U., on the change of potential of the substance.

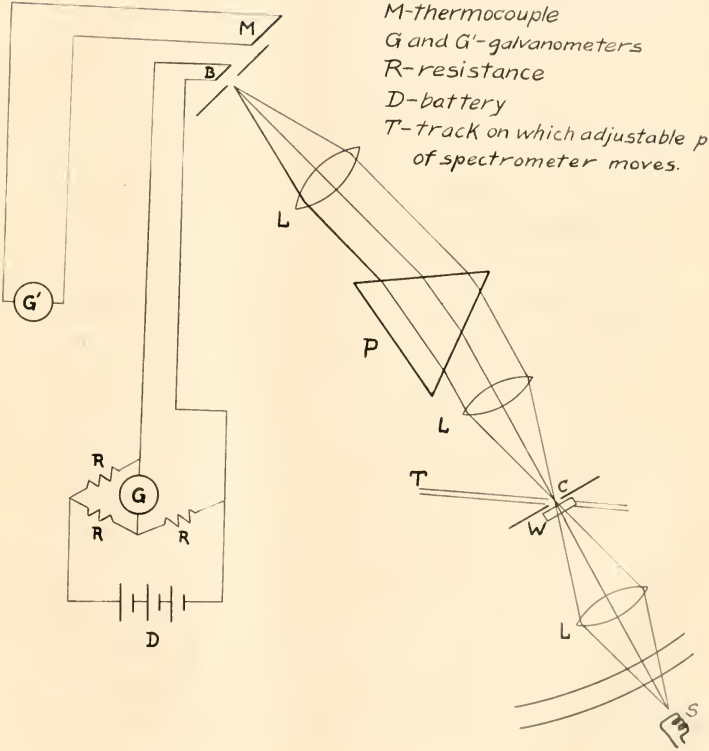
Apparatus.

The same apparatus was used for the two substances.

1. The apparatus used for determining the change in the electrical resistance produced by different wave-lengths of light, in the region 6000 to 4000 A.U. for Cu_2O and 9000 to 4000 for Selenium, is indi-

FIG. I.

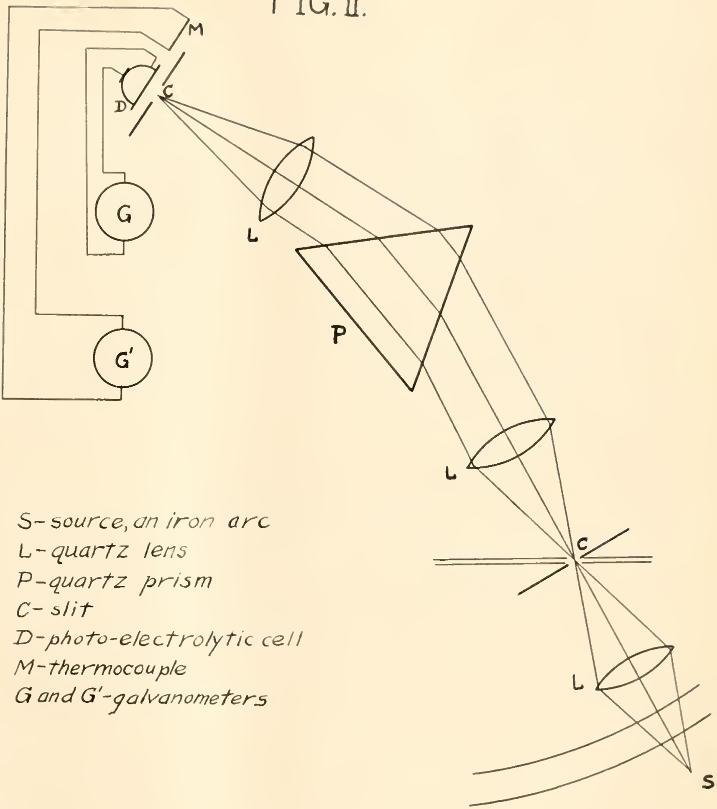
S-source, a tungsten lamp.
L-quartz lens
P-quartz prism
C-slit
W-water cell
B-selenium or cuprous oxide
M-thermocouple
G and G'-galvanometers
R-resistance
D-battery
T-track on which adjustable part of spectrometer moves.



cated in Figure I. The source of light was a small tungsten lamp of 32 candle power. The spectrometer that was used has been accurately described by A.H.Pfund (1). The water cell was inserted to cut out the strong heat rays. An orange glass screen was used as an opaque screen for wave-lengths shorter than 4650 A.U.; so that the measured changes in resistance would be unaffected, as much as possible, by scattered light.

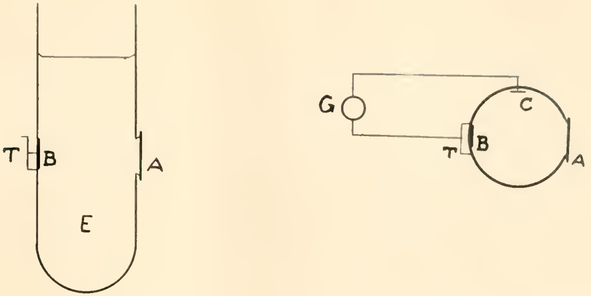
2. The apparatus used for determining the photo-electrolytic effect produced by the different regions of the spectrum in the range 8700 to 2500 A.U. is indicated in Figure II. The source of light was an iron arc. The substance to be investigated was sealed into the side of the glass cell, as shown in Figure III. B represents the substance, which is opposite a quartz window A. Great difficulty was experienced in obtaining a good electrical contact to B; but this was finally overcome by sealing a small copper sheet directly behind B, and filling the space between the copper and B, with mercury. The other electrode of the cell was, in some cases, a sample of the same substance as B, sealed into the side of the tube in such a position that the light could not reach it. In other cases, a platinum wire, or zinc strip immersed in the solution formed the other electrode. The solution was distilled water, when working with Cu_2O; whereas a few drops of nitric acid were added to the distilled water when working with selenium. The two electrodes were joined to the terminals of a high resistance galvanometer.

FIG. II.



S- source, an iron arc
L- quartz lens
P- quartz prism
C- slit
D- photo-electrolytic cell
M- thermocouple
G and G'- galvanometers

FIG. III.



Vertical Section of Photo-electrolytic Cell

Horizontal Section of Photo-electrolytic Cell

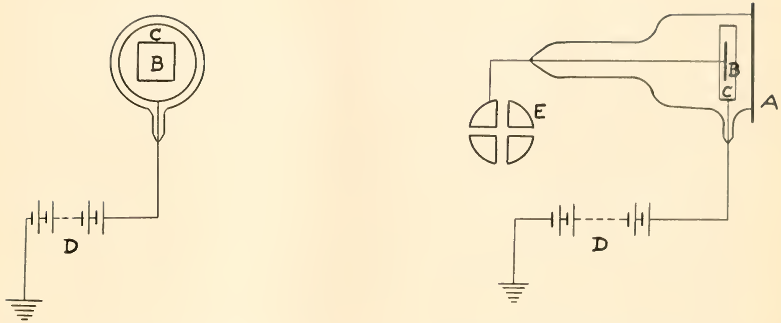
A-quartz window
B-selenium or cuprous oxide
C-other electrode
E-electrolyte
T-trough holding mercury
which makes contact with B.

3. The apparatus used for determining the longest wave-length that will cause a photo-electric effect of the substance is indicated in Figure IV. The photo-electric cell was enclosed in an earthed-tin case, which was connected by a brass pipe to the brass case containing the electrometer. A small hole was cut in the tin case to allow the light to fall on the cell. The source of light was an aluminium spark, when working with Cu_2O, and an iron arc when working with selenium. This light was focussed on the substance in the cell, by means of a quartz lens.

Method.

1. In determining the change of resistance produced by different wave-lengths of light, the Wheatstone Bridge was balanced as closely as possible with the substance, not illuminated, as the unknown resistance. The reading of the galvanometer, g, was taken. Then by means of the spectrometer, a given region of the spectrum of the tungsten lamp was allowed to fall on the substance, and the steady deflection of the galvanometer, g, was read. The change of resistance was found to be independent of the length of time of illumination, unless that time was very short. Thus the substance was illuminated until the resistance had reached a constant value. Then by a screen the illumination was cut off. The reading of the galvanometer was taken before and after the illumination of the substance, and the average of these readings was taken as the zero from which the deflection was measured. In most cases, there was no zero shift. The method was repeated for the differ-

FIG. IV



Vertical Section of Photo-electric Cell

Horizontal Section of Photo-electric Cell

A-quartz window
B-selenium or cuprous oxide
C-copper cylindar
D-battery of 112 volts
E-quadrant electrometer

ent regions throughout the spectrum, and thus the steady change in resistance produced by the various regions of the spectrum of the tungsten lamp, was measured. A.H.Pfund (1) showed for Cu_2O, and Nicholson (2) showed for selenium, that for any monochromatic portion of the spectrum for which the light is not transmitted by the substance, the change in resistance is proportional to the square-root of the intensity of the source. Thus to study the comparative effects of radiations of different wavelengths, it is advisable to divide the change of resistance produced by a definite portion of the spectrum by the square-root of its relative intensity. It was necessary, therefore, to obtain the intensity distribution of the spectrum of the source. This was done by taking the steady deflection of the galvanometer, g', when the thermo-couple, which was made to replace the resistance cell in position, was illuminated successively by each region of the spectrum. The galvanometer readings were taken before and after each illumination of the thermocouple, and the average of these readings was taken as the zero, from which the deflection was measured. The zero shift was at times quite large, but in these cases, a great many sets of readings were taken. It is assumed that the steady deflections of the galvanometer, g', are proportional to the corresponding intensity of the radiation falling on the thermo-couple. This is found to be justified, since the results obtained in this way are exactly the same as those obtained by A.H.Pfund (1) for Cu_2O, where he allowed monochromatic radiation of equal intensities, throughout the whole spectral region

investigated to fall on the substance, whose change in resistance was being measured.

2. In determining the photo-electrolytic effect produced by the different regions of the spectrum, the cell was exposed to the different regions by a quartz spectrometer, and the corresponding throws of the galvanometer were observed. These throws were proportional to the change in potential produced in the substance. The galvanometer readings were taken before and after each illumination of the substance, and the average of these was taken as the zero from which the deflection was measured. There was usually no zero shift. Thus the change in potential produced by the various regions of the spectrum of the iron arc was measured. By a separate experiment, to be described later, it was shown that for the unresolced radiation, the change in potential produced is proportional to the intensity of the radiation, in the case of Cu_2O; and is proportional to the two-thirds power of the intensity of the radiation in the case of selenium. It is assumed that the same law holds for the monochromatic radiations that are not transmitted by the substance. Thus to study the comparative effects of radiations of different wave-lengths it is advisable to divide the change of resistance produced by a definite portion of the spectrum by the relative intensity, 1, in the case of Cu_2O, and by $I^{\frac{2}{3}}$ in the case of selenium. It was necessary therefore, to obtain the spectral energy distribution of the iron arc. This was obtained by means of the thermocouple, exactly as the spec-

tral energy distribution of the tungsten light was obtained, as described in (1). In some cases, the changes in potential were determined alternately with the intensity for each portion of the spectral region; while in other cases, the change in potential was determined for each portion of the region investigated, and then the intensity for each portion, without adjusting the arc. Both methods gave the same results.

To determine the relation between the change in potential produced, and the intensity of the source, the unresolved radiation of a 32 c.p. tungsten lamp was focussed on the specimen, and a rotating sector was placed directly in front of the photo-electrolytic cell. The throw of the galvanometer was obtained when the sector was not rotating. The galvanometer reading was taken before and after the cell was illuminated, and the average of these readings was taken as the zero from which the deflection was measured. This method was repeated, when the sector was rotating, and completely open, that is, allowing one half as much light to fall on the cell as in the previous case. This method was repeated again when the rotating sector was one-half open, and again when it was one-fourth open. It was observed that the effect varied directly as the intensity of the incident radiation for Cu_2O, and directly as the two-thirds power of the intensity of the incident radiation for selenium, as shown in the following table:

Table I.

Relative Intensity	Observed change of potential of Cu_2O	Calculated change of potential of Cu_2O	Observed change of potential of Se.	Calculated change of potential of Se.
I	20		48.3	
$\frac{1}{2}$ I	10.05	10.0	32.2	30.43
$\frac{1}{4}$ 1	5.2	5.0	23.85	19.17
$\frac{1}{8}$ I	2.7	2. 5	14.86	12.08

3. In determining the long wave-length limit that will cause the photo-electric effect, screens of various thicknesses of glass were made, and when that screen was found, which would give a very small deflection of the electrometer, its transmission spectrum was taken. Thus the shortest wave-length that it transmitted was the longest wave-length that would cause the photo-electric effect of the substance.

Results for Cuprous Oxide.

1. The observed change of resistance of Cu_2O produced by radiations of different wave-lengths in the region 6000 to 3900 A.U. was exactly in accord with the work done by A.H.Pfund (1).

A typical set of data is recorded in Table I.

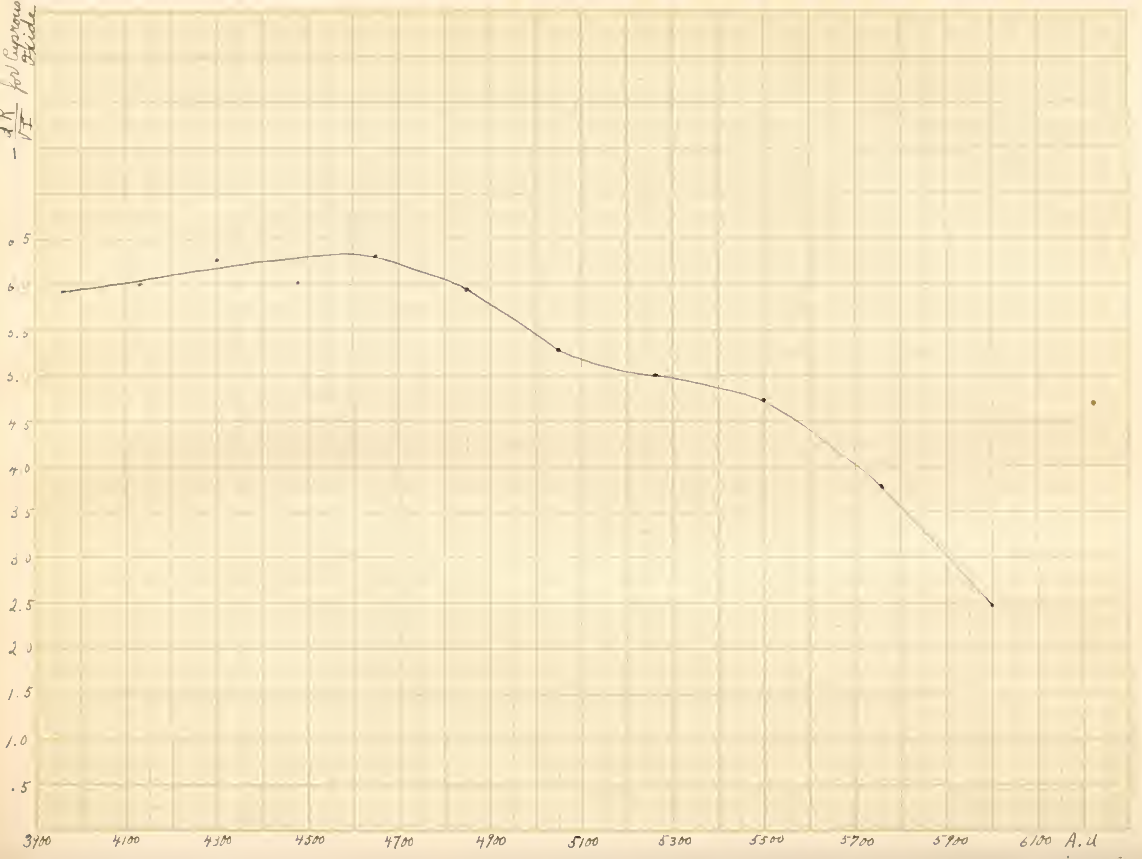
Table 1.

Wave-length in A.U.	Change of Resistance = - dR	Relative intensity of Radiation. I	$\sqrt{I}$	$\frac{-dR}{\sqrt{I}}$
3960	2.65	.2	.447	5.92
4130	3.12	.27	.52	6.0
4300	3.87	.40	.63	6.28
4480	4.17	.48	.69	6.04
4650	5.12	.65	.81	6.32
4850	5.95	1.0	1.0	5.95
5050	6.60	1.55	1.25	5.28
5260	7.57	2.27	1.51	5.0
5500	8.55	3.25	1.80	4.75
5760	8.07	4.55	2.13	3.79
6000	6.35	6.59	2.57	2.49

The final results are shown in Fig. 5, in which the ratio of the change of resistance to the square-root of the relative intensity of the radiation is plotted against the corresponding wave-length of light.

It will be noted in the graph that there is a slight maximum at 4600 A.U.; and from A.H.Pfund's work, which extended the investigation further into the ultra-violet a large maximum occurs at about 2800 A.U.

2. The effect of wave-length on the change of potential


$-\frac{dK}{\sqrt{I}}$ for Cuprous Oxide
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
3900
4100
4300
4500
4700
4900
5100
5300
5500
5700
5900
6100
A.U

of the Cu_2O in an electrolytic cell has been observed by A.H. Pfund and E. Karrer; but the results were never published. The readings obtained in this investigation confirm their results.

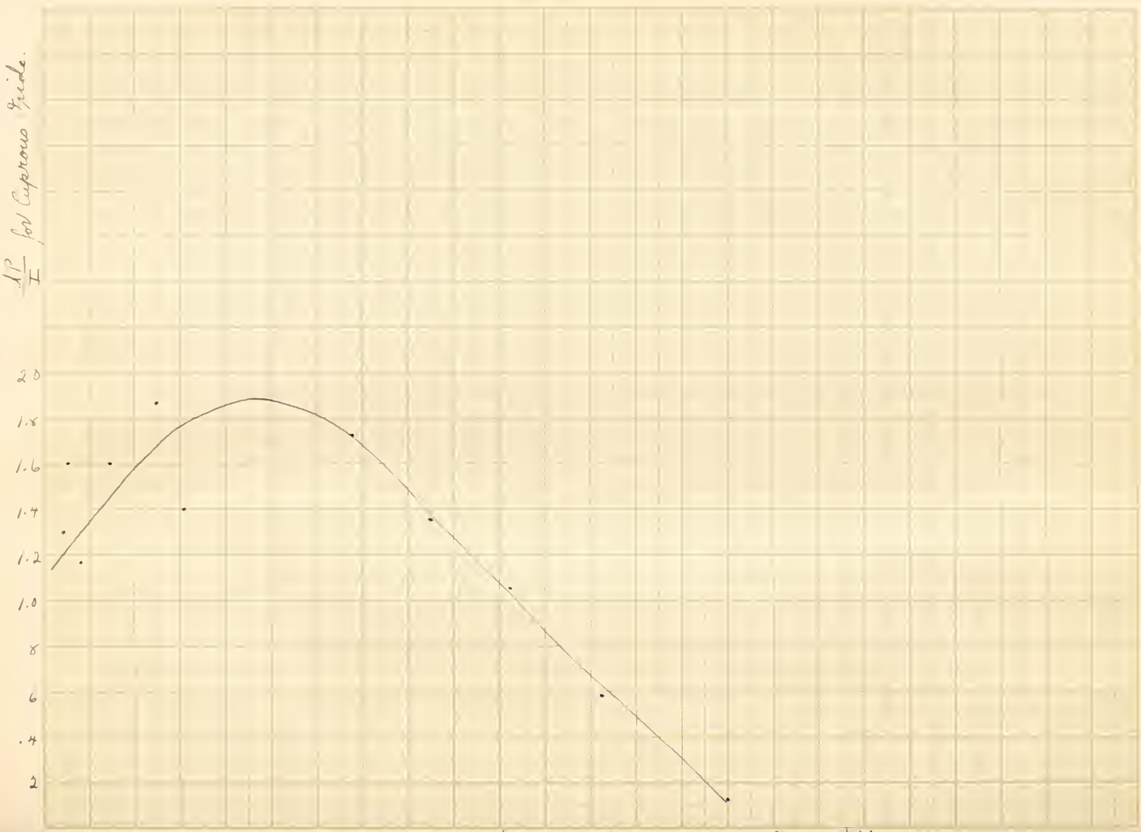
A typical set of data is recorded in Table II.

Table II.

Wave-length in A.U.	Change of Potential dP	Relative Intensity of Radiation I	$\frac{dP}{I}$
2690	.75	.55	1.3
2710	.80	.50	1.6
2770	1.10	.85	1.17
2890	.8	.5	1.6
3100	1.50	1.2	1.87
3220	1.0	.75	1.4
3960	1.9	1.1	1.72
4300	3.5	2.7	1.35
4650	2.0	1.9	1.05
5050	1.5	2.55	.58
5500	.3	2.45	.122

The final results are shown in Fig. VI, in which the ratio of the change of potential to the relative intensity of radiation is plotted against the corresponding wavelength.

It will be noted from the graph that there is a maximum effect at about 3500 A.U., and that the effect continues throughout the


$\frac{\Delta P}{I}$ for Cuprous Oxide.

ultra-violet region to 2600 A.U., that is, as far as the region was investigated.

This potential effect was observed when the back of the Cu_2O plate was illuminated, that is , when the light did not pass through the electrolyte, but fell on that of the Cu_2O plate which was in contact with the air.

The absolute magnitude of the potential effect was determined by connecting the galvanometer to a potentiometer, and finding the potential that would cause the same deflection as that given by the effect of 3500 A.U. on the Cu_2O. By this means, it was found that the change of potential produced in the Cu_2O by 3500 A.U. of intensity as obtained from the iron arc, was of the order of magnitude of 10^{-5} volts.

T.W.Case (3) has investigated the effect of light on one electrode of a cuprous oxide voltameter, with copper formate as the electrolyte. In the unresolved radiation of sunlight, a much more intense source than was used in this present experiment, he obtained 0.11 volts for the full intensity. But in his work he found that the illuminated Cu_2O plate has its potential lowered; whereas, in the present investigation, the illuminated Cu_2O plate was made positive as the result of illumination, the current flowing from this plate to the dark electrode through the external circuit.

3. The photo-electric effect of Cu_2O has been observed by E.H. Kennard and E.O. Dieterich (4) ; but the long wave-length limit was not

determined. However, R.A.Millikan (5) records the long wave-length limit for copper oxide to be 2535 with a possible error of 50 A.U. The long wave-length limit as obtained in the present investigation was 2572 A.U.

Several pieces of Cu_2O were investigated. They showed the same long wave-length limit for the photo-electric effect, and the same characteristic photo-electrolytic action; but, although a particular specimen would show a large photo-electrolytic action, it did not necessarily show a measurable change of resistance with exposure to light.

Results for Selenium.

1. The observed changes of resistance of selenium produced by radiation in different regions of the spectrum in the range of 9000 to 4000 A.U. were exactly in accord with the results obtained by Nicholson. (2)

A typical set of data is recorded in Table III.

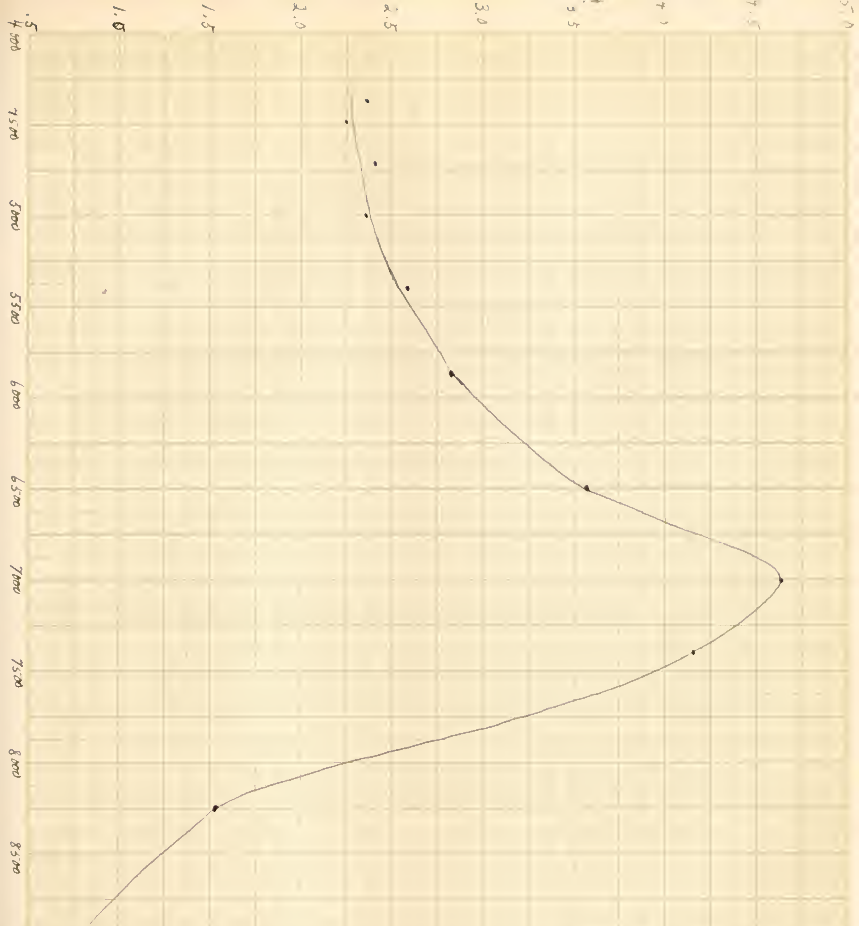
Table III.

Wave-length in A.U.	Change in Resistance = -dR	Relative I intensity of Radiation I	I	$\frac{-dR}{I}$
4370	.760	.10	.316	2.37
4480	.79	.12	.346	2.25
4720	1.11	.21	.458	2.41
5000	1.49	.40	.6325	2.36
5400	2.17	.71	.8426	2.58
5870	3.23	1.30	1.14	2.83
6500	5.5	2.37	1.54	3.57
7000	8.36	3.23	1.80	4.64
7400	8.57	4.29	2.06	4.16
8250	3.84	6.29	2.50	1.53
9100	1.8	6.37	2.52	.71

The final results are shown in Fig. VII in which the ratio of the change of reistance to the square root of the relative intensity of the radiation is plotted against the corresponding wave-length of light.

It will be noted in the graph that there is a sharp maximum at 7000 A.U., and from Nicholson's work, which extended the investigation further into the ultra-violet, a slight maximum is found to occur also at about 4500 A.U.

2. The change of potential of the selenium in an electrolytic


.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
4500
4750
5000
5500
6000
6500
7000
7500
8000
8500
9000
A. U.

cell when the other electrode is platinum has been observed by Minchin (6). In the present investigation a very much larger effect was observed when the other electrode was a strip of zinc; but this was probably due to the smaller internal resistance of the cell, when the large zinc electrode was used.

A typical set of data, for a cell with selenium and zinc as electrodes, in distilled water, with a few drops of nitric acid added, is recorded in Table IV. Care was taken that the light did not fall on the zinc. The direction of the current obtained is from the illuminated selenium to the dark electrode through the external circuit; that is, the selenium is raised to a higher potential, by action of the light.

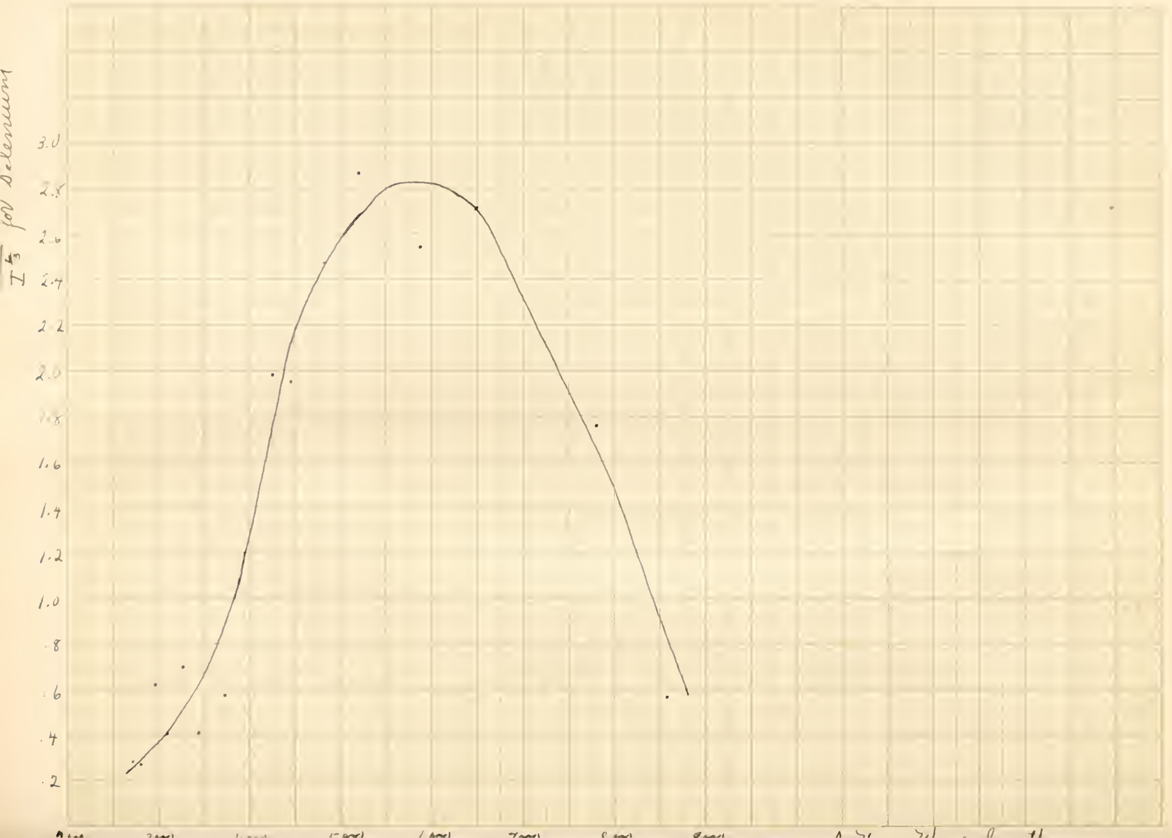
The final results are shown in Fig. VIII in which the ratio of the change of potential divided by the two-thirds power of the relative intensity of the radiation is plotted against the corresponding wave-lengths.

It will be noted from the graph that there is a decided maximum at about 5700 A.U.

Table IV.

Wave-lengths in A.U.	Change of Potential dP	Relative Intensity of Radiation. I	$\frac{dP}{I}$
2710	.3	1.1	.28
2800	.4	1.8	.27
2970	.7	1.2	.62
3100	.6	1.8	.406
3280	.7	1.0	.7
3450	.8	2.7	.41
3740	1.8	5.5	.577
3950	3.0	5.8	.93
4260	5.0	4.0	1.98
4480	4.5	3.5	1.95
4830	4.3	2.3	2.47
5200	7.6	4.3	2.87
5870	8.4	6.0	2.54
6500	10.4	7.5	2.71
7800	11.1	15.8	1.76
8750	5.5	30.3	.566

4. The photo-electric effect of selenium has been studied by E.H.Kennard and E.O.Dieterich (4), but the long-wave-length limit was not determined. The long wave-length limit as obtained in the


$I^{\frac{1}{3}}$ for Selenium
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2

present investigation was 2260 A.U.

Several pieces of selenium were investigated. They showed the same long wave-length limit for the photo-electric effect, and the same characteristic photo-electrolytic action; but, although a particular specimen would show a large photo-electrolytic action, it did not necessarily show a measurable change of resistance with exposure to light.

Discussion.

It has been the purpose of this paper to observe the above-mentioned three effects of light on the same sample, with a view to aiding in the theoretical interpretation of these and other experimental facts.

The fact that for both cuprous oxide and selenium, the photo-electrolytic effect begins at a wave-length shorter than the resistance effect, and that the photo-electric effect begins at a wave-length shorter than the photo-electrolytic, indicate that least energy is required to simply excite the electrons (assuming Thomson's doublet theory of resistance, since it was found to explain some of the experiments of A.H. Pfund (1)), and that a greater amount of energy is required to remove an electron from the substance, and thus raise its potential. Also the greater the dielectric constant of the medium surrounding the substance, the less the amount of energy necessary to remove the electron. The concept is, however, complicated by the fact that the photo-electrolytic effect is observed, whether the

part of the substance in contact with the liquid or the part of the substance in contact with the air is illuminated.

It is of interest to note that the photo-electric effect of Cu_2O begins at approximately 2570 A.U., and that the ratio $-dR/\sqrt{I}$ begins to decrease at approximately 2800 A.U., having been steadily increasing up to this point. That these two effects should occur at the same wave-length, is what would be expected on Thomson's doublet theory of resistance, due to electrons being ejected completely from the substance. The slight discrepancy in the long wave-length limit for the photo-electric effect, and the maximum in the change of resistance effect, may be due to the fact that when measuring the change of resistance, the Cu_2O is in air, which has a slightly higher dielectric constant than a vacuum, and as we have seen in the two cases observed, the greater the dielectric constant, the less the energy necessary to eject the electron completely from the substance. The fact that this agreement is not found in the case of selenium may be due to the fact that there are so many different forms of selenium, and that they pass so readily from one to another. To attempt any further physical interpretation is inadvisable, until more data have been obtained.

Summary.

1. (a) The long wave-length limit that will cause a change of resistance of Cu_2O is greater than 6400 A.U.
   (b) The long wave-length limit that will cause the photo-electrolytic effect of Cu_2O is about 5600 A.U.

(c) The long wave-length limit that will cause the photo-electric effect of Cu_2O is about 2570 A.U.

2. (a) The long wave-length limit that will cause a change of resistance of selenium is about 10,000 A.U.

   (b) The long wave-length limit that will cause the ohoto-electrolytic effect of selenium is 9500 A.U.

   (c) The long wave-length limit that will cause the photo-electric effect of Cu_2O is about 2260 A.U.

3. The photo-electrolytic effect was observed in Cu_2O for both front and back illumination, the front of the Cu_2O being in contact with distilled water, and the back of the Cu_2O being in contact with air.

4. In the photo-electrolytic action for both cuprous oxide and selenium, the potential of the substance is raised.

5. The maximum photo-electrolytic effect, i.e. the ratio of the photo-electrolytic effect to the relative intensity of radiation, of cuprous oxide is at approximately 3500 A.U.

6. The maximum photo-electrolytic effect, i.e. the ratio of the photo-electrolytic effect to the two-thirds power of the relative intensity of radiation for selenium is at approximately 5700 A.U.

7. The photo-electrolytic effect of cuprous oxide varies directly with the intensity of the source, for unresolved radiation.

8. The photoe-electrolytic effect of selenium varies directly with the two-thirds power of the intensity of the source, for unresolved radiation.

In conclusion I desire to express my appreciation to Professor Ames and to the entire Graduate Physics department of the Johns Hopkins University for the interest they have taken in the work. I especially want to thank Dr. Pfund, who suggested the problem, and so cheerfully aided me in every possible way.

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Biographical Note.

Vola Price Barton, daughter of James S. and Irene (Eichelberger) Barton, was born in Baltimore, Maryland, December 19, 1893. She received her early education in the Baltimore public schools. In 1915 she received the degree of Bachelor of Arts from Goucher College. The years 1915-1917 were spent at Mount Holyoke College as a graduate student, and as an assistant in Physics. In 1917 she received the degree of Master of Arts from Mount Holyoke College. The year 1917-1918 she was Assistant in Physics at Goucher College.

In the fall of 1918 she entered the Johns Hopkins University as a graduate student, and did part time work during the years 1918-1922. The year 1918-1919 she was Assistant in Physics at Goucher College; and for the years 1919-1922 she was Instructor in Physics at Goucher College. The year 1922-23 she spent in residence at the Johns Hopkins University. She followed the courses of Professors Ames, Wood and Pfund in Physics, Professor Murnaghan in Mathematics, and Professor Reid in Geophysics.

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